

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶: A01N 31/02	A1	(11) International Publication Number: WO 99/11123 (43) International Publication Date: 11 March 1999 (11.03.99)
(21) International Application Number: PCT/US98/18263 (22) International Filing Date: 2 September 1998 (02.09.98) (30) Priority Data: 60/056,279 3 September 1997 (03.09.97) US (71) Applicant (for all designated States except US): S. C. JOHNSON & SON, INC. [US/US]; 1525 Howe Street, Racine, WI 53403 (US). (72) Inventor; and (75) Inventor/Applicant (for US only): CONWAY, Mary, J. [US/US]; 823 Wolff Street, Racine, WI 53402 (US). (74) Agents: BOZEK, Laura, L. et al.; Patent Section, S. C. Johnson & Son, Inc., 1525 Howe Street, Racine, WI 53403 (US).		(81) Designated States: AU, BR, CA, CZ, HU, KG, KZ, MX, NZ, PL, RU, SI, SK, UA, US, UZ, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: METHOD OF DISINFECTING AND INHIBITING MOLD AND MILDEW GROWTH ON NON-POROUS HARD SURFACES (57) Abstract A method of cleaning, disinfecting, and inhibiting mold and mildew growth on a non-porous hard surface such as glass, ceramic tile, glazed porcelain, fiberglass, Formica® and plastic, utilizing a composition comprising an aliphatic alcohol; at least one organic ether, and optionally a secondary alcohol.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

METHOD OF DISINFECTING AND INHIBITING MOLD AND MILDEW GROWTH ON NON-POROUS HARD SURFACES

5

Priority

This application claims the benefit of U. S. Provisional Application No. 60/056, 279, filed September 3, 1997.

10

Technical Field

This invention relates to aqueous cleaning, sanitizing, disinfecting and mold and mildew inhibiting compositions for non-porous hard surfaces such as glass (e.g., mirrors and shower doors), glazed porcelain, metallic (e.g., chrome, stainless steel, and aluminum), ceramic tile, enamel, fiberglass, Formica®, Co-
15 rian® and plastic. The compositions utilize surprisingly low concentrations of particular alcohols as well as advantageously leave very low levels of residue on the surface.

20 Background Art

Complete elimination of pathogenic micro-organisms on various surfaces, especially hard surfaces where such organisms may stay active for relatively long periods of time, has long been a goal of those charged with cleaning and main-
25 taining in an antiseptic fashion kitchens and bathrooms in the home, as well as in commercial and institutional settings such as hospitals, medical clinics, hotels and restaurants. A further goal has been to prevent the formation of allergens caused by the growth of mold and mildew on bathroom surfaces.

30 A variety of chemical disinfecting agents have been developed to accomplish these goals. However, some of these agents have disadvantages in that some are corrosive, unpleasant to smell or capable of staining certain surfaces that commonly need to be cleaned and disinfected. Additionally, if the agents are volatile organic compounds, the compositions are environmentally disadvanta-
35 geous when utilized at higher concentrations. Furthermore, some disinfecting agents contain components which leave residual solids on surfaces such as

glass, polished tile, or metals which detract from the visual appearance of these surfaces.

Chlorine bleaches such as aqueous sodium hypochlorite have long been
5 recognized as being effective against all types of micro-organisms, provided that
the bleach is used in sufficiently high concentrations, such as 5,000 ppm (0.5%)
of active sodium hypochlorite and higher, depending on the micro-organism to be
eliminated. These types of solutions are recommended for use for disinfecting an
area where blood or other potentially pathogenic biological contaminants have
10 been spilled or released and total disinfection is required. At such high levels of
sodium hypochlorite, the sensory irritation from the chlorine smell from the bleach
simply makes this agent undesirable for routine cleaning and disinfection of, for
example, hospital rooms, where patients remain in the room during and after the
cleaning and disinfection process.

15

Disadvantageously, hypochlorites may also stain or degrade some sur-
faces such as Formica®. Additionally, bleaches demonstrate high reactivity with
other cleaning agents. For example, bleach when combined with ammonia pro-
duces harmful chloramine gas. Also, bleach when combined with an acid based
20 cleaner produces chlorine gas, which is potentially hazardous.

Consumers are also highly sensitive to streaking and hazing which may
develop on windows, shower doors and mirrors, and the like. A desirable cleaner
should produce a surface which exhibits little or no change in clarity and optical
25 properties from the moment of use and ideally remain that way for weeks and
months. In the context of the present invention, streaking can be defined as a
visible diffractive layer which causes light scattering. Hazing can be described as
a misty diffractive layer that covers the entire surface developing instantly or over
time, which clouds the surface. Most cleaning products leave behind a thin
30 residual film of product in intimate contact with the surface. Hydrogen bonding to
the surface oxides and/or hydroxides with continuous attachment produces an
optically clear film. Small breaks or disruptions in these continuous residual films
cause diffractive streaks which are visible to the naked eye. Similarly, residual
diffractive particles will also be visible to the naked eye. Specific formulation

techniques are required to maintain the integrity of a homogeneous residual film and to eliminate residual diffractive particles on the cleaned surface.

Chemical and optical stability of the residual surface film may be achieved
5 by maintaining a proper balance of surfactants and coupling agents in the formula. More typically, however, the formulator will prepare a cleaning composition to ensure stability of the composition and the delivery of good disinfecting properties without considering the residual film properties and optical effects. For example, Quaternary ammonium compounds have long been recognized as being
10 useful for their antibacterial properties, as can be seen from U.S. Pat. Nos. 3,836,669 to Dadekian; 4,320,147 to Schaeufele; 4,336,151 to Like et al.; 4,444,790 to Green et al.; 4,464,398 to Sheets et al.; and 4,540,505 to Frazier. However, quaternary ammonium compounds have a tendency to contribute to visible streaking on glass and other surfaces.

15

An additional disadvantage of quaternary ammonium based compositions is that the addition of common highly efficacious cleaning surfactants such as anionic surfactants is not possible due to incompatibility. Accordingly, more costly surfactants must be employed in quaternary ammonium formulations.

20

Further, quaternary ammonium compounds are known eye and skin irritants, thus special care must be taken by the user of compositions employing these compounds.

25

To minimize expense, undesirable odors and possible detrimental effects of disinfecting agents on surfaces to be disinfected, it is desirable to minimize the amount of disinfecting or mold and mildew inhibiting agents used while still retaining efficacy. As will be explained in greater detail below, it has been found that a combination of specific alcohols, and glycol ethers at a pH in the range of from
30 about 4.0 to about 13.0 provides a composition that is effective as a cleaner, disinfectant and a mold and mildew prevention agent on non-porous hard surfaces.

35

Disclosure of Invention

One object of this invention is to provide compositions that can be used in a method of cleaning and disinfecting various surfaces. Another object of this invention is to provide such compositions that inhibit mold and mildew growth on
5 surfaces.

A particularly advantageous object of this invention is to provide compositions that can be used in household, commercial and institutional settings for cleaning and disinfection purposes that are more tolerable to people remaining in
10 the area disinfected because the smell of the compositions is more appealing to the user than if highly concentrated hypochlorite bleach compositions were used as the active disinfectant. Yet another object is to provide cleaning, disinfecting and mold and mildew inhibiting compositions that do not have high concentrations of certain compounds which are prone to corrode or stain surfaces to be treated.

15 Further, it is an object of this invention to provide disinfectancy and mold and mildew inhibition on surfaces at reduced levels of environmentally disadvantageous volatile organic compounds.

20 Another object of the invention is to provide a method of using the composition as a rinsing aid to maintain a clean and disinfected shower and prevent the build-up of undesirable deposits on shower surfaces.

Additionally, it is an object of the present invention to reduce the potential
25 of disinfecting compositions to cause visible streaks on glass and polished surfaces when compared to disinfectants containing quaternary ammonium compounds.

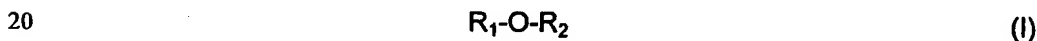
These and other objects of the present invention are provided by applying
30 to a non-porous hard surface, an effective amount of an aqueous cleaning composition comprising an aliphatic alcohol, a glycol ether or ethers, and optionally, a secondary alcohol selected from the group consisting of monohydric alcohols, dihydric alcohols, trihydric alcohols and polyhydric alcohols, at a pH in the range of from about 4.0 to about 13.0. The composition may also contain
35 other conventional materials including, but certainly not limited to; surfactants,

chelating agents, pH modifiers, hydrotropes, fragrances, dyes, etc. Surprisingly, these compositions provide cleaning, disinfectancy and mold and mildew inhibiting properties at significantly reduced levels of volatile organic compounds without the need for chlorine bleaches, quaternary ammonium or phenolic compounds.

The first component of the present invention is an aliphatic alcohol. Exemplary aliphatic alcohols include isopropanol, propanol, butanol and ethanol. The preferred aliphatic alcohol is isopropanol, due to its evaporation and low odor characteristics. Methyl alcohol, however, is less favored due to its toxicity.

Typically the aliphatic alcohol is utilized in an amount of up to about 10%; preferably from about 1.0 % to about 10.0%; and most preferably from about 3.5% to about 10.0% by weight of the composition (hereinafter, all amounts are given in weight percent, unless specified otherwise).

A further component of the present invention is an organic ether. The organic ethers according to the present invention are represented by the following Formula (I):



wherein R_1 is a C_1 - C_8 linear, branched, or cyclic alkyl or alkenyl optionally substituted with -OH, -OCH₃, or -OCH₂CH₃, and R_2 is a C_1 - C_6 linear, branched or cyclic alkyl or alkenyl substituted with -OH.

Preferably, R_1 is an optionally substituted C_3 - C_6 alkyl or alkenyl, and R_2 is a monosubstituted C_2 - C_4 linear or branched alkyl or alkenyl.

More preferably, R_1 is an unsubstituted or monosubstituted linear or branched C_3 - C_6 alkyl, and R_2 is a monosubstituted C_2 - C_4 linear or branched alkyl.

Most preferably, R_1 is an unsubstituted n - C_3 - C_4 or n - C_6 linear alkyl or -CH₂CHCH₃, and R_2 is -CH₂CH₂OH or -CH₂CHCH₃.



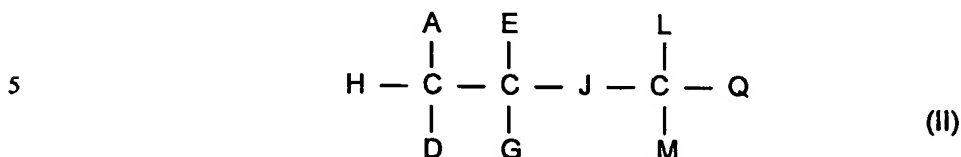
The preferred organic ethers are the glycol ethers. Suitable glycol ethers include ethylene glycol n-hexyl ether, (available as Hexyl Cellosolve®, from Union Carbide Corporation), ethylene glycol mono-butyl ether (available as Butyl Cellosolve®, from Union Carbide Corporation, or as Dowanol® EB, from Dow Chemical Co.), dipropylene glycol methyl ether (available as Dowanol® DPM, from Dow Chemical Co.), propylene glycol n-butyl ether (sold as Dowanol® PnB), propylene glycol tertiary-butyl ether (available as Arcosolv® PTB from Arco Chemicals), and propylene glycol n-propyl ether (available as Dowanol® PnP from Dow Chemical Co.). Other useful glycol ethers include other P-series glycol ethers such as propylene glycol methyl ether (sold as Dowanol® PM), dipropylene glycol n-Butyl Ether (sold as Dowanol® DPnB), and dipropylene glycol n-Propyl Ether (sold as Dowanol® DPnP) and mixtures thereof.

In the present invention, the glycol ether(s) are generally present in the range from about 0.01 to about 10.0 total weight percent. Preferably, the glycol ether component is employed in the range from about 0.5% to about 10.0%; and most preferably, from about 0.9% to about 8.0% by weight of the composition, depending upon the specific glycol ether.

Ideally the glycol ether component is a mixture of ethers, each present in a range of from about 0.01% to about 10%. Preferably the composition comprises 1.2% or less by weight of ethylene glycol n-hexyl ether and from about 0.01% to about 10.0%, more preferably from about 0.01% to about 3.0% by weight of ethylene glycol n-butyl ether. With respect to the Hexyl, it has been found beneficial to use this component at or near its solubility limit of 1.0% in an aqueous solution.

It has been found that certain alcohols couple with the nonvolatile organic ethers above, and markedly reduce the potential for the formation of visible streaks. These secondary alcohols include various monohydric alcohols, dihydric

alcohols, trihydric alcohols, and polyhydric alcohols. Suitable secondary alcohols for use in the present invention are represented by the following Formula (II):



wherein A, D, E, G, L and M are independently -H, -CH₃, -OH or -CH₂OH; J is a single bond or -O-; and Q is -H or a straight chain C₁-C₅ alkyl optionally substituted with -OH, with the proviso that:

- (i) if Q is not an alkyl substituted with -OH, then at least one of A, D, E, G, L and M is -OH or -CH₂OH;
- (ii) when only one of A and E is -OH and J is a single bond, D, G, L, M and Q may not be -H simultaneously;
- (iii) when A, D, E, G and L are -H simultaneously, J is a single bond and M is -CH₂OH, Q may not be -H or -CHCH₂CH₂CH₃; and

$$\begin{array}{c}
 | \\
 \text{OH}
 \end{array}$$
- (iv) when J is single bond, none of E, G, L and M is -CH₃ or -CH₂OH and Q is -CH₂CH₂CH₂CH₃, then at least two of A, D, E, G, L and M are -OH; or at least one of A and D is -CH or -CH₂OH.

Preferably, at least one of A, D, E and G is -OH or -CH₂OH and Q is -H or a straight chain C₁-C₅ alkyl optionally monosubstituted with -OH.

More preferably, one or two of A, D, E and G is -OH or -CH₂OH and Q is -H or -CH₂OH.

Most preferably, one or two of A, D, E and G is -OH or -CH₂OH, J is -O-, L and M are independently -H or -CH₃ and Q is -CH₂OH. The most preferred secondary alcohol has been found to be propylene glycol.

In the present invention, the secondary alcohol will be generally employed in the range of up to about 5.0%; preferably from about 0.1% to about 3.5%; and most preferably, from about 0.2% to about 2.5% by weight of the composition.

5 Compositions of the present invention typically have a pH of about 4 or above, more preferably from about 7 to about 13 and ideally from about 9.5 to about 12.5. The pH may be adjusted by conventional pH adjusting agents such as citric acid, acetic acid, sodium hydroxide, potassium hydroxide, ammonia and mixtures thereof.

10

The compositions utilized in the present invention are typically water-based for reasons of household safety and commercial acceptance. Soft, distilled or deionized water are preferred as the source of water for dilution of the individual components as well as for the water added as the balance of the
15 composition for such use as an aqueous shower rinsing solution.

Generally, the amount of water utilized is dependent on the particular application of the composition. For household disinfecting compositions, water is typically present in an amount from about 1.0% to about 95%; preferably 50% to
20 about 95%; and most preferably from about 85% to about 95% by weight of the composition.

Builder salts and chelating agents of the type conventionally used in liquid detergent compositions for cleaning hard surfaces may also be included in the
25 compositions of the present invention in small amounts, generally less than about 5%, provided that they do not promote streaking on surfaces. Such builder salts include sodium sesquicarbonate, sodium carbonate, sodium gluconate, sodium citrate, sodium borate, potassium carbonate, tetrapotassium pyrophosphate, sodium metasilicate and the like, and such polymeric materials as polyacrylic acid.
30 The chelating agents may include water soluble chelating agents such as alkali metal or substituted ammonium amino polycarboxylates such as sodium or potassium salts of ethylenediamine tetraacetic acid ("EDTA") such as tetrasodium EDTA.

The compositions according to the present invention may contain one or more surfactants to adjust the surface tension of the composition and to aid in cleaning. These surfactants may include anionic surfactants such as sodium dodecyl benzene sulfonate, decyl (sulfophenoxy) benzenesulfonic acid disodium salt sold by Dow Corp. as Dowfax® C10L, and sodium lauryl sulfate, or amphoteric surfactants such as caprylic glycinate sold by Witco Corp. as Rewoteric® AMV. The anionic surfactant may also be a fluoro anionic surfactant such as 3M Fluorad® FC-129. Other suitable surfactants include betaine surfactants such as coco amido propyl dimethyl sultaine sold by Lonza Corp. as Lonzaine® CS, coconut based alkanolamide surfactants sold by Mona Chemicals as Monamid® 150-ADD or nonionic surfactants including the ethoxylated alcohols such as Neodol® 23-3 and Neodol® 23-5 (Shell Chemicals), alkyl phenol ethoxylates, and Igepal CO-630 (Rhone-Poulenc); low foaming surfactants such as lauramine oxide sold by Lonza Corp. as Barlox® LF and cleaning surfactants such as ethoxylated vegetable oil sold by GAF Corp. as Emulphor® EL-719.

It is believed that the use of cationic amphoteric surfactants may result in cleaners which have a tendency for streaking or smearing problems. Accordingly, amphoteric surfactants used in the present invention are preferably employed under alkaline conditions to render the anionic portion of the amphoteric compound active.

Ideally, the amphoteric surfactant exhibits high detergency and low foam characteristics. Suitable examples of such amphoteric compounds include a capryloamphodipropionate such as Amphoterger® KJ-2 (Lonza Corp.) which has a lipophilic end with a chain length including the amide carbon of C₆ (4%); C₈ (57%); C₁₀ (38%) and C₁₂ (1%).

The amphoteric surfactants may desirably be utilized in their salt-free forms to maximize their compatibility in the cleaning systems, particularly if the cleaner contains detergents.

In the present invention, the surfactant(s) will be employed in the range from 0 to about 5.0%; preferably in the range of from about 0.01% to about 3.0%; and most preferably in the range of from about 0.01% to about 2.0% by weight of the composition.

5

The formulator may also choose to include one or more cleaning solvents or cleaning supplements such as monoethanolamine. These cleaning solvents will typically be utilized in amounts from 0 to about 2.0%, preferably from about 0.01% to about 1.0% and most preferably, from about 0.125% to about 0.8% by weight of the composition.

Thickening agents may also be utilized where there is a need to increase the time the consumer can wipe the composition before it runs down a vertical surface. Suitable thickening agents include polyacrylic acid polymers and copolymers such as Carbopol® ETD 2623 (B. F. Goodrich Co.) or Accusol 821 (Rohm and Haas).

For better consumer acceptance, the glass cleaning composition will typically contain colorant or dye, such as Direct Blue 86, or polymeric colorants such as Liquitint® Blue HP and a fragrance component. If a dye or a fragrance is contained in the composition, it may be preferable also to include an anti-oxidant, such as potassium iodide, to protect these materials and provide sufficient stability for a long shelf life. If the fragrance oil utilized which is not already preblended with a solubilizer, a fragrance solubilizer, such as Igepal-CO 630 commercially available from Rhone-Poulenc, or an alkoxylated linear alcohol such as Poly-Tergent SL-62 from Olin Chemical, is preferably utilized in a 50:50 blend with the fragrance. Of course, it is certainly possible for commercial or other reasons to provide a clear or fragrance-free composition by omitting these materials.

30

MODES OF CARRYING OUT THE INVENTION

The following Examples are provided to show various aspects of the present invention without departing from the scope and spirit of the invention. Unless

otherwise indicated, all parts and percentages used in the following Examples are by weight.

Generally, the compositions can be prepared by blending the ingredients
5 in any order. It is preferred that if the fragrance does not contain a solubilizer, a 50:50 preblend of these components is added to the composition. It is also desirable to prepare the compositions of the present invention by first admixing the surfactant component (if utilized), water and at least a portion of the alcohols before incorporating the glycol ether(s). Preferably the components are admixed
10 with stirring to hasten dissolution. Mixing is done at ambient temperature.

The following ingredients were used in the compositions described in the Examples:

15 Ammonium Hydroxide (28%) - ammonium hydroxide solution at 28% ammonia concentration.

Caustic Soda (50%) - aqueous solution of sodium hydroxide at 50% active concentration.

20 Sodium Docecyl Benzene Sulfonate (36%) - aqueous solution of sodium docecyl benzene sulfonate at 36% active concentration.

Example 1

An aqueous antibacterial composition according to the present invention was prepared according to the following formula:

5	Sodium dodecyl benzene sulfonate	0.2000
	Isopropanol, anhydrous	3.5000
	Ethylene glycol n-hexyl ether	0.9000
	Ethylene glycol mono-butyl ether	1.0000
	Ammonium hydroxide	0.3000
10	Propylene glycol	0.2500
	Fluorad® FC-129 fluoro surfactant	0.0200
	Fragrance with solubilizer (50:50 blend)	0.0500
	Caustic soda	0.0600
	Soft Water	balance

15

This formula has a pH in the range of about 11.5 to about 12.2. When tested for use as an antibacterial composition, all tested slides/carriers of staphylococcus aureus showed no indication of bacterial growth after treatment. This composition was also tested using deionized water rather than soft water, and found to be
20 equally effective. When reformulated to eliminate the ammonium hydroxide, no loss of effectiveness was noted.

Example 2

An aqueous shower rinsing composition according to the present invention was prepared according to the following formula:

5	Sodium dodecyl benzene sulfonate	0.2000
	Isopropanol, anhydrous	3.5000
	Ethylene glycol n-hexyl ether	0.9000
	Ethylene glycol mono-butyl ether	1.0000
10	Igepal® CO-630, fragrance solubilizer	0.0250
	Propylene glycol	0.2500
	Fluorad® FC-129 fluoro surfactant	0.0200
	Fragrance	0.0250
	Caustic soda, 50% active	0.0600
15	Deionized Water	balance

This formula has a pH in the range of about 11.5 to about 12.2.

Comparative Example 2A

20 A commercially available cleaning product sold under the tradename Clean Shower was analyzed and is believed to have the following composition:

	Ethoxylated Fatty ester (surfactant)	0.7000
	Ethylenediaminetetracetic Acid salts	1.2000
25	Isopropyl alcohol	2.4000
	Fragrance	Present
	Ammonia	Present
	Water	balance

The pH of this product was measured as 4.9.

Comparative Example 2B

A commercially available cleaning product sold under the tradename Tilex Fresh Shower was analyzed and is believed to have the following composition:

5

Ethoxylated Fatty ester (surfactant)	1.80
Ethylenediaminetetracetic Acid salts	1.10
Isopropyl alcohol	2.20
Fragrance	Present
10 Ammonia	Present
Water	balance

The pH of this product was measured as 11.4.

The aqueous shower rinsing compositions of Examples 2, 2A and 2B are applied onto shower surfaces after showering to prevent the build-up of deposits such as soap scum, minerals, germs, bacteria, mold and mildew. These examples were also tested for antibacterial effect, as in Example 1. Of these
5 Examples, Example 2 passed this test, while Examples 2A and 2B failed in terms of antibacterial efficacy.

In addition to the above comparative Examples, additional tests were conducted to evaluate the effectiveness of several shower rinsing compositions
10 for ability to reduce soap scum residue. A standard soap scum solution was prepared by weighing a specified amount of Racine Wisconsin tap water (approximately 125 ppm calcium carbonate) into a large beaker. The water was heated to 160°F, and specified amounts of bath soap, shampoo plus conditioner, shave gel, synthetic sebum, Bandy Black clay were added. The solution was
15 mixed well for ten minutes, then cooled to 120°F before application to tile test surfaces. Four tile by three tile black ceramic tile boards were used as test surfaces. Glossmeter readings were taken on clean tiles before treatment, using a conventional gloss meter. To simulate a shower, four sprays of room temperature tap water were sprayed on the tile surface. After waiting one minute,
20 four sprays of soap scum solution were applied evenly to the tile test surface. After one minute, four strokes of comparative example formulation were evenly applied and allowed to air dry. After the tile surfaces had dried, this was considered to be one application. For purposes of the test, a total of seven applications were made. Gloss meter readings were taken of the tiles after seven
25 application, and the change in gloss (gloss of clean tiles minus the gloss of the test tiles after seven applications) was calculated. The compositions tested are as follows.

TABLE 1

Raw Material	Example 1	Example 2C	Example 2D	Example 2E	Example 2F	Example 2G
Deionized Water		92.23	93.87	93.85	92.34	94.13
Monoethanolamine		0.20				
Acusol 445N				0.02		
Acusol 820					0.03	
Soft Water	93.72	0.00	0.00	0.00	0.00	0.00
SDBS	0.20	0.40	0.40	0.40	0.40	0.20
Flourad FC-129	0.02	0.02	0.02	0.02	0.02	0.02
Hexyl Cellosolve	0.90	1.20	1.20	1.20	1.20	0.90
Butyl Cellosolve	1.00	3.00	2.00	2.00	3.00	1.00
Propylene Glycol	0.25	1.00	0.50	0.50	1.00	0.25
Ammonium Hydroxide	0.30	0.00	0.00	0.00	0.00	0.00
Isopropanol	3.50	1.90	1.90	1.90	1.90	3.50
Caustic Soda, 50%	0.06	0.00	0.06	0.06	0.06	0.00
Firmenich Fragrance		0.05	0.05	0.05	0.05	
Measure pH	11.7	NA	NA	NA	NA	3.96
Fragrance to be added	0.05	OMIT	OMIT	OMIT	OMIT	OMIT
	100.00	100.00	100.00	100.00	100.00	100.00

The results of the residue testing, using the gloss readings as taught above, are as follows;

<u>Example:</u>	<u>Change in Gloss:</u>
Example 2C	1.50
Example 2G	2.80
Example 2F	3.00
Example 2E	4.34
Example 2D	4.48
Example 2	8.66
No Treatment	31.48
Example 2A	31.78
Example 2B	33.63

5

As can be seen, as compared to tile surfaces which received "No treatment", the formulae of this invention (Examples 2, and 2C - 2G) showed significantly lower values for the change in gloss, indicating that less residue was left behind. On the other hand, the competitive examples (Examples 2A and 2B) showed no difference in change of

10 gloss from the untreated tile samples.

Preferably, the consumer should begin with a clean shower surface before beginning to use the shower rinsing compositions of the present invention, as the

rinsing composition is not a shower cleaner as traditionally utilized, but is a daily maintenance system for keeping showers clean and sanitary with a minimum of consumer effort. However, if the consumer begins treating soiled shower surfaces with the rinsing composition, the results will not likely be apparent for about
5 2 to 4 weeks, assuming that the product is used daily as instructed.

It is believed that the rinsing composition is best sprayed onto the shower surfaces with a conventional trigger sprayer or pressurized dispenser, or through shower head metering, preferably before any undesirable deposits dry and set.
10 In subsequent showers, the water and mist from showering enhances the removal of deposits. Thus, the repeated cycles of spray application of shower rinsing composition, drying of shower surfaces, and subsequent showering serve to convey deposits via gravity (with the rinsing composition as the carrier) down to the shower drain.

15

Water rinsing other than the showering itself can be done, but is unnecessary. No wiping, scrubbing, or other mechanical action is necessary, in contrast to conventional cleaning agents which are used to remove deposits only after such deposits have dried. However, wiping may enhance the performance of the
20 rinsing composition.

Furthermore, in contrast to simply rinsing the shower surfaces with plain tap water which typically leaves deposits, the rinsing composition of the present invention air-dries spot free with reduced visible streaking. The rinsing composition is also effective in maintaining bathtub surfaces and metallic bathroom fixtures substantially free of deposits.
25

Example 3:

A disinfecting composition according to the present invention was prepared according to the following formula:

5		
	Sodium dodecyl benzene sulfonate	0.2000
	Isopropanol, anhydrous	3.5000
	Ethylene glycol n-hexyl ether	0.9000
	Ethylene glycol n-butyl ether	1.0000
10	Ammonium Hydroxide	0.3000
	Propylene glycol	0.2500
	Fluorad® FC-129 fluoro surfactant	0.0200
	Caustic soda, 50% active	0.0600
	Soft Water	balance

15

BACTERIA TESTING:

Example 3 was tested by the AOAC Germicidal Spray Test and determined to be
 20 efficacious against the following test systems at a 10 minute contact (exposure)
 time:

25	<i>Staphylococcus aureus</i> /ATCC 6538
	<i>Salmonella choleraesuis</i> /ATCC 10708
	<i>Pseudomonas aeruginosa</i> /ATCC 15442
	<i>Escherichia coli</i> /ATCC 43890
	<i>Enterococcus (Streptococcus) faecalis</i> /ATCC 19433
	<i>Listeria monocytogenes</i> /ATCC 15313
30	<i>Pastuerella multocida</i> / ATCC 43137
	<i>Shigella dysenteriae</i> /ATCC 29026
	<i>Shigella flexneri</i> /ATCC 25875
	<i>Shigella sonnei</i> /ATCC 25931
	<i>Yersinia enterocolitica</i> /ATCC 9610
35	<i>Enterococcus (Streptococcus) faecalis</i> /ATCC 51299
	<i>Campylobacter fetus</i> /ATCC 27374

VIRUS (DISINFECTING) TESTING

Example 3 is efficacious against the following viruses at a 10 minute contact (exposure) time when tested by the ASTM E1053-91 test method:

5

Herpes simplex virus type 1
Herpes simplex virus type 2
Influenza virus type A2
Human Immunodeficiency Virus Type 1 (HIV)

10

MOLD TEST

The composition of Example 3 was tested against *Aspergillus Niger* ATCC 6275 by the EPA Hard Surface Mildew-Fungistatic Test and found to control or inhibit
15 the growth of mold and mildew on hard surfaces.

SANITIZER TEST

The composition of Example 3 was also tested by the "Sanitizer for Inanimate,
20 Non-Food Contact Surfaces" test method prepared by the Registration Division, Office of Pesticide Programs, EPA, 1976. (DIS/TSS Guideline 10 dated Jan 7, 1982.) The composition of Example 3 was found to be efficacious as a non-food contact sanitizer at a one minute contact (exposure) time.

Example 4:

A series of 57 additional compositions in accordance with the present invention were prepared and tested for antibacterial effect, in accordance with the
 5 AOAC Germicidal Spray Test, at a 10 minute contact time. Unless indicated otherwise, the samples contained 0.9% Hexyl and 1.0% Butyl. The results of these tests are set forth in the Tables which follow. Abbreviations used in these tables are as follows:

	butyl or but	ethylene glycol mono-butyl ether
10	hexyl or hex	ethylene glycol n-hexyl ether
	pg	propylene glycol
	IPA	isopropyl alcohol
	PnB	propylene glycol n-butyl ether
15	PtB	propylene glycol t-butyl ether

The AOAC (Association of Official Analytical Chemists) Germicidal Spray Test, 15th Edition 1990, section 961.02, was used to screen various formulations using 10 carriers per composition. The formulations were tested at a ten
 20 minute contact time against *Staphylococcus aureus* ATCC 6538. If 0, 1, 2, or 3 failures per ten carriers were obtained, the compositions were considered to be effective. Four or five failures per ten carriers indicated borderline efficacy when tested. Six to ten failures indicated a product was not effective.

25 . Samples in which Hexyl was present in concentrations above 0.6% were effective, in the presence of Butyl. While the presence of Butyl appeared to increase the efficacy of other ethers to which it was added, inconsistent results were obtained when PnB and PtB were utilized. These glycols exhibited antibacterial properties only in the presence of Hexyl, up to concentrations of 5%
 30 of PnB. While it is not fully understood at this time, it has been found that when Hexyl is employed as the glycol ether component, it is necessary to have at least 0.01% Butyl present, and further, efficacy of the Hexyl does not become pronounced until the concentration of Hexyl exceeds 0.6% regardless of the concentration of Butyl with it. Conversely, the effectiveness of Butyl appears to
 35 be as an adjunct to another glycol ether, unless the concentration of Butyl exceeds 5%.

TABLES 2A, B, C

Hexyl/Butyl Effects:

	no hexyl	0.10% hexyl	0.50% hexyl	0.60% hexyl	0.70% hexyl	0.80% hexyl
Observations/Results:	126-2	126-9	126-14	126-52	126-53	126-54
pH	11.59	11.59	11.54	11.42	11.39	11.38
color	none	none	none	none	none	none
appearance	clear	clear	clear	clear	clear	clear
Micro results(# not passing)	10	10	19	5	3	0
# of plates/slides tested on	10	10	20	10	10	10
Micro retest(# not passing)			10			
# of plates/slides tested on			10			

	no butyl	0.01% butyl	0.05% butyl	0.10% butyl	0.50% butyl	3.0% butyl	5.0% butyl
Observations/Results:	126-1	126-47	126-48	126-8	126-49	126-28	126-28
pH	11.60	11.39	11.47	11.58	11.38	11.54	11.52
color	none	none	none	none	none	none	none
appearance	clear	clear	clear	clear	clear	clear	clear
Micro results(# not passing)	9	0	0	5	0	1	1
# of plates/slides tested on	10	10	10	10	10	10	10
Micro retest(# not passing)	15			18			
# of plates/slides tested on	30			30			

	no hex/but	0%hex 5%but	.2%hex 1.7%but	.4%hex 1.5%but	.6%hex 1.3%but	.8%hex 1.1%but	1%hex .9%but
Observations/Results:	126-41	126-51	126-42	126-43	126-44	126-45	126-46
pH	11.44	11.43	11.43	11.41	11.46	11.40	11.38
color	none	none	none	none	none	none	none
appearance	clear	clear	clear	clear	clear	clear	clear
Micro results(# not passing)	10	10	10	9	4	1	1
# of plates/slides tested on	10	10	10	10	10	10	10
Micro retest(# not passing)							
# of plates/slides tested on							

From the above, it may be seen that samples in which Hexyl was present in concentrations above 0.6% were effective, in the presence of at least 0.01% Butyl. While not fully understood, it appears that there is a synergism between the Hexyl and Butyl, since neither is effective without the other. Further, it is

noted that when Hexyl and Butyl are used together, efficacy is not achieved until the Hexyl concentration is 0.6 or above.

TABLE 3

Propylene Glycol Effects:

	no pg	0.10% pg	1.0% pg	3.0% pg	5.0% pg
Observations/Results:	126-3	126-12	126-15	126-27	126-31
pH	11.59	11.59	11.57	11.57	11.55
color	none	none	none	none	none
appearance	clear	clear	clear	clear	clear
Micro results(# not passing)	1	3	3	1	2
# of plates/slides tested on	10	10	10	10	10
Micro retest(# not passing)	2				3
# of plates/slides tested on	10				10

5

From TABLE 3, above, one may conclude that the presence of propylene glycol is not critical to success of the present invention, but as previously indicated, its inclusion is beneficial for purposes of reduction of residue and streaking.

From TABLE 4, which follows, P-series glycol ethers are effective below
 10 5%, when used in combination with Hexyl in a concentration above 0.6%. At concentrations of 5% or higher, the presence of Hexyl appears to be unnecessary in the case of propylene glycol n-butyl ether (PnB).

15

TABLE 4

P-Series Glycol Ether Effects:

Observations/Results:	2.0% PnB no hexyl	2.0% PnB no butyl	0.10% PnB, no hex/but	2.0% PnB, no hex/but	5.0% PnB, no hex/but	2.0% PTB no hexyl	2.0% PTB no butyl	0.10% PTB, no hex/but	2.0% PTB, no hex/but	0.05 PTB, no hex/but
	126-22	126-20	126-10	126-24	126-29	126-23	126-21	126-11	126-25	126-30
pH	11.57	11.63	11.58	11.62	11.66	11.62	11.72	11.65	11.57	11.59
color	none	white	none	none	none	none	none	none	none	none
appearance	clear	milky	clear	clear	clear	clear	clear	clear	clear	clear
Micro results(# not passing)	10	0	10	10	1	10	1	10	9	10
# of plates/slides tested on	10	10	10	10	10	10	10	10	9	10
Micro retest(# not passing)					2					
# of plates/slides tested on					10					

TABLE 5 A and B

Primary Alcohol Effects:

	no IPA	1.0% IPA	2.00% IPA	5.0% IPA	10.0% IPA
Observations/Results:	126-4	126-16	126-55	126-32	126-36
pH	11.50	11.53	11.38	11.55	11.69
color	none	none	none	none	none
appearance	clear	clear	clear	clear	clear
Micro results(# not passing)	5	5	1	2	0
# of plates/slides tested on	10	10	10	10	10
Micro retest(# not passing)	23				
# of plates/slides tested on	30				

	1.0% propanol no IPA	5.0% propanol no IPA	10.0% propanol no IPA	1.0% butanol no IPA	5.0% butanol no IPA	10.0% butanol no IPA	1.0% ethanol no IPA	5.0% ethanol no IPA	10.0% ethanol no IPA
Observations/Results:	126-17	126-33	126-37	126-18	126-34	126-38	126-19	126-35	126-39
pH	11.37	11.39	11.42	11.52	11.52	11.54	11.52	11.52	11.62
color	none	none	none	none	white	white	none	none	none
appearance	clear	clear	clear	clear	milky	milky	clear	clear	clear
Micro results(# not passing)	4	0	0	2	0	0	5	3	1
# of plates/slides tested on	10	10	10	10	10	9	10	10	10
Micro retest(# not passing)									
# of plates/slides tested on									

5

The presence of an aliphatic alcohol has been found to be beneficial, with the most benefit being obtained at concentrations above about 2% of isopropyl alcohol and above 5% for each of propanol, butanol, and ethanol.

TABLE 6

Miscellaneous Effects:

	no Flourad	0.01% Flourad	no NaOH	0.20% NaOH	no NH3 1.03 g Citric	no NH3 1.20 g Citric	no NH3 1.06 g Citric
Observations/Results:	126-5	126-7	126-6	126-13	126-40A	126-40B	126-40C
pH	11.56	11.59	10.47	12.19	8.98	8.05	7.04
color	none	none	none	none	none	none	none
appearance	clear	clear	clear	clear	clear	clear	clear
Micro results(# not passing)	3	2	1	1	1	3	0
# of plates/slides tested on	10	10	10	10	10	10	10
Micro retest(# not passing)	0						
# of plates/slides tested on	10						

Observations/Results:	Example 2C	Example 2D	Example 2E	Example 2F	Example 2G
pH	NA	NA	NA	NA	3.96
color	none	none	none	none	none
appearance	clear	clear	clear	clear	clear
Micro results(# not passing)	0	1	1	0	1
# of plates/slides tested on	10	10	10	10	10

The compositions of the present invention are equally effective for antibacterial activity both with and without the fluorosurfactant utilized. Efficacy is demonstrated at pH varying from about 4 to about 13.

Further to the above testing for antibacterial effect, the composition of Example 3 was compared with a commercially available competitive glass and surface cleaner and a commercially available competitive all purpose disinfectant. The comparison of streaking, or residue left on surface was conducted by applying a measured amount of each of the compositions to a black glass surface, removing the composition by wiping with a cheesecloth wiper, allowing the glass to dry for 15 minutes, and then evaluating both visually and by reflectometer. It was found that by both measures, the composition of Example 3 was significantly superior in terms of streaking and deposit of residue.

INDUSTRIAL APPLICABILITY

The compositions of the present invention are simple to produce and use. The compositions can be applied to surfaces to be disinfected in a variety of ways
5 such as by sponging, spraying, mopping, wiping, foaming, dipping and in various other ways that are commonly used for conventional disinfecting and cleaning agents. The compositions may be also be dispensed from conventional pump, trigger or aerosol dispensers. The compositions may also be dispensed from sponges or towelettes which are pre-moistened with the compositions.

10

Thus the compositions of the present invention will find use as multipurpose disinfectants for many surfaces needing disinfection such as countertops, work areas, rest rooms, mirrors, shower doors and the like. The compositions can also be utilized to inhibit mold and mildew growth. Additionally,
15 the compositions provide good detergency and streak-resistance on glass and polished surfaces.

Although the present invention has been illustrated with reference to certain preferred embodiments, it will be appreciated that the present invention is
20 not limited to the specifics set forth therein. Those skilled in the art will readily appreciate numerous variations and modifications within the spirit and scope of the present invention, and all such variations and modifications are intended to be covered by the present invention.

We Claim:

1. A method for removal of micro-organisms from a hard surface, said method comprising contacting said surface with a composition comprising an aliphatic
5 alcohol and a glycol ether.
2. A method as set forth in Claim 1, wherein said composition further comprises a secondary alcohol selected from the group consisting of monohydric alcohols, dihydric alcohols, trihydric alcohols, and polyhydric alcohols.
10
3. A method as set forth in Claim 2, wherein said secondary alcohol comprises propylene glycol.
4. A method as set forth in Claim 1, wherein said glycol ether is selected from the
15 group consisting of ethylene glycol n-hexyl ether, ethylene glycol mono-butyl ether, and mixtures thereof.
5. A method as set forth in Claim 4, wherein said aliphatic alcohol is isopropyl alcohol.
20
6. A method for disinfecting a surface, said method consisting of applying to said surface an effective amount of an aqueous cleaning composition comprising an aliphatic alcohol, an organic ether, a secondary alcohol selected from the group consisting of monohydric alcohols, dihydric alcohols, trihydric alcohols and
25 polyhydric alcohols, at a pH in the range of about 7 to about 13.0, and leaving said composition in contact with said surface for longer than 10 minutes.
7. A method as set forth in Claim 6, wherein said organic ether comprises a glycol ether selected from the group consisting of ethylene glycol n-hexyl ether,
30 ethylene glycol mono-butyl ether, and mixtures thereof.
8. A method as set forth in Claim 7, wherein said aliphatic alcohol is isopropanol, and said secondary alcohol is propylene glycol.

9. A method set forth in Claim 8, further comprising a surfactant.

10. A method for sanitizing a surface, said method consisting of applying to said
5 surface an effective amount of an aqueous cleaning composition comprising an
aliphatic alcohol, an organic ether, a secondary alcohol selected from the group
consisting of monohydric alcohols, dihydric alcohols, trihydric alcohols and
polyhydric alcohols, at a pH in the range of about 7 to about 13.0, and leaving
said composition in contact with said surface for longer than 1 minute.

10

11. A method as set forth in Claim 10, wherein said organic ether comprises a
glycol ether selected from the group consisting of ethylene glycol n-hexyl ether,
ethylene glycol mono-butyl ether, and mixtures thereof.

15 12. A method as set forth in Claim 11, wherein said aliphatic alcohol is
isopropanol, and said secondary alcohol is propylene glycol.

13. A method set forth in Claim 12, further comprising a surfactant.

20 14. A method as set forth in Claim 10, wherein said surface comprises a shower
surface.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 98/18263

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 A01N31/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 97 29173 A (JOHNSON & SON) 14 August 1997 see examples 1-8 see page 4, line 15 - page 6, line 32 ---	1-14
P,X	GB 2 319 179 A (RECKITT & COLMAN) 20 May 1998 see page 1, line 7 - page 3, line 15 see page 8, line 18 - page 9, line 14 see examples 1,2 ---	1,2,4,5
X	EP 0 647 706 A (THE CLOROX COMPANY) 12 April 1995 see page 2, line 30 - page 4, line 23 see examples 1-10 --- -/--	1-14



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

27 November 1998

Date of mailing of the international search report

07/12/1998

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Fort, M

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 98/18263

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 463 735 A (STONEBRAKER ET AL.) 26 August 1969 see the whole document ----	1-14
X	GB 1 311 534 A (MONTY KROY PAGE) 28 March 1973 see the whole document ----	1,4
X	WO 93 16162 A (THE CLOROX COMPANY) 19 August 1993 see page 2, line 16 - line 30 see page 6, line 29 - page 7, line 33 see examples 1,2,6-10 ----	1,4
X	WO 93 25654 A (UNILEVER) 23 December 1993 see page 4, line 11 - page 6, line 14 -----	1,4

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 98/18263

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9729173 A	14-08-1997	NONE	
GB 2319179 A	20-05-1998	AU 4341897 A WO 9821305 A	03-06-1998 22-05-1998
EP 0647706 A	12-04-1995	US 5468423 A CA 2133889 A CN 1106454 A PL 305351 A US 5523024 A US 5817615 A ZA 9407821 A	21-11-1995 09-04-1995 09-08-1995 18-04-1995 04-06-1996 06-10-1998 25-05-1995
US 3463735 A	26-08-1969	NONE	
GB 1311534 A	28-03-1973	NONE	
WO 9316162 A	19-08-1993	US 5252245 A CA 2107889 A CN 1076476 A DE 69310622 D DE 69310622 T EP 0580838 A ES 2102011 T MX 9300648 A PL 172561 B US 5468423 A US 5437807 A US 5523024 A US 5817615 A ZA 9300683 A	12-10-1993 08-08-1993 22-09-1993 19-06-1997 04-09-1997 02-02-1994 16-07-1997 29-07-1994 31-10-1997 21-11-1995 01-08-1995 04-06-1996 06-10-1998 06-09-1993
WO 9325654 A	23-12-1993	AU 678360 B AU 4318493 A CZ 9403195 A DE 69302384 D DE 69302384 T EP 0647264 A ES 2087743 T HU 70082 A JP 7507584 T SK 154894 A AU 678170 B AU 4708593 A CA 2143108 A CZ 9500492 A DE 69310750 D DE 69310750 T WO 9404644 A EP 0656936 A ES 2103483 T HU 71957 A JP 8500376 T PL 307685 A SK 24595 A US 5403515 A ZA 9305771 A	29-05-1997 04-01-1994 17-05-1995 30-05-1996 26-09-1996 12-04-1995 16-07-1996 28-09-1995 24-08-1995 11-07-1995 22-05-1997 15-03-1994 03-03-1994 12-07-1995 19-06-1997 11-09-1997 03-03-1994 14-06-1995 16-09-1997 28-02-1996 16-01-1996 12-06-1995 11-07-1995 04-04-1995 09-02-1995